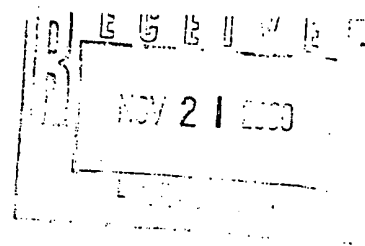


German Patent No. 896 189



Job No.: 397-80168

Translated from German by the Ralph McElroy Translation Company  
910 West Avenue, Austin, Texas 78701 USA

Ref.: AEROGEL TRANSLATIONS

FEDERAL REPUBLIC OF GERMANY  
GERMAN PATENT OFFICE  
PATENT NO. 896 189

Granted on the Basis of the First Transition Law of July 8, 1949 (WiGBI., p. 175)

Class: 12 g  
Group: 4 01  
Filing No.: S 19821 IV b / 12 g  
Date Issued: November 9, 1953

Patented in the Federal Republic of Germany as of September 29, 1950

Patent Application Published on June 11, 1952

Notification of Granting of Patent Published on October 1, 1953

Priority of the applications in the United States of America of October 9, 1942, April 22, 1943 and April 24, 1945 has been claimed

METHOD FOR PRODUCING SILICIC ACID-CONTAINING GEL PARTICLES

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The invention refers to a method for producing silicic acid-containing gel particles with adsorbent and catalytic properties from a gel-forming hydrosol of an inorganic oxide. The goal of the invention consists of producing gel particles with a surface as smooth and hard as possible and with largely spherical shape.

As is known, such gel particles are used in various ways, for example for drying gases by adsorption, as water-softening zeolites, as catalysts, etc., in particular as catalysts for conversion of hydrocarbons. In general, reaction vessels that are filled with the gel particles are used in this case, and a heavy hydrocarbon oil, for example, is passed through the vessel for conversion to

gasoline. Since the catalytic effect of the gel particles that act as catalysts drops off after a certain amount of time, the catalysts have to be regenerated, which means that the reaction chamber will be idle. In order to obtain reasonably continuous operation, it is for this reason necessary to provide a number of reaction vessels, which are continuously switched to conversion operation and to regeneration. This is a complicated mode of operation. For this reason completely continuous operation for such processes that operate with a catalyst can be achieved by moving the catalyst in circulation, thus continuously withdrawing it from the reaction vessel and sending it to a reaction vessel, from which the catalyst is again returned to the reaction vessel after it has been regenerated. This circulation puts a not inconsiderable mechanical strain on the catalyst; it is subject to considerable abrasion, and gel particles that are not sufficiently strong can crumble due to pressure and shock.

In producing gel particles for the said purposes it is possible to operate in a simple way so that a large coherent gel mass is made and then broken up in order to obtain the desired gel particles. In this case the breaking operation must be followed by screening in order to obtain particles of the sizes that are desired in each case, which results in a great deal of loss. Another known proposal provides for molding the gel while still wet. However, this is very complicated and requires costly molding equipment, the continuous cleaning of which gives rise to considerable costs. Finally dividing the gel mass, drying and size reducing one part and using the other wet part to bind the size reduced part by means of a molding operation, which is likewise very complicated, is also known.

With the method in accordance with the invention the gel-forming hydrosol, while being divided into individual droplets, is introduced into a liquid or gaseous medium that is immiscible with water and the hydrosol, which is kept at a temperature under the boiling point of the hydrosol and in which the droplets remain until the gel has formed. In the conversion of the hydrosol to the hydrogel within the said medium the droplets, as a consequence of surface tension compared to the medium, have taken on an essentially spherical shape, so that the hydrogel that forms and, after drying, the gel particles are obtained in the form of small spheres. The term spherical form here should also be understood to mean sphere-like shapes such as flattened or flat spheres, where it is crucial that these spherical gel particles have a smooth uniform surface. This form of gel particle is seen as an ideal shape for all catalyst processes that are possibilities, regardless of whether they are processes involving fixed bed or moving catalysts. The spherical gel particles always uniformly arrange themselves in the reaction vessel, and it is impossible to form channels within the catalyst masses through which the liquids or vapor to be treated can flow at an elevated rate. Also, in the case of a catalyst circulating from reaction vessel to regeneration vessel and back, the spherical shape guarantees absolutely uniform flow of the catalyst.

Another advantage of the method in accordance with the invention lies in the fact that the resulting gel particles are extraordinarily hard and resistant to stress. Particles that are produced when the spheres are broken also retain this hardness, so that even broken particles can be used for conversion of hydrocarbons.

The method is carried out, for example, so that the hydrosol is introduced from above into a mineral oil layer that is on top of a water layer so that the droplets pass through the oil layer by the force of gravity, during which gel formation takes place, while the formed gel particles after reaching the water layer are removed via a flow of water within the layer. The generation of the hydrosol with gel-forming properties takes place immediately before introduction of the hydrosol into the oil layer, by mixing the necessary reactant solutions, for example sodium silicate and an acid solution, with each other in a mixing nozzle, where the concentration and mixture ratio are chosen so that gel formation does not take place within the mixing device, but rather does not begin until after the mixture has left the mixing device, and is completed before the droplets leave the oil layer. Instead of oil, it is also possible to use, for example, crude potassium, kerosene, etc., as the medium. The hydrosol can also be introduced into a gaseous atmosphere or into air, so that a method such as is known in the case of drying by spraying into a drying tower results. In this case gel particles that are uniformly dried up to 10-50% water content are formed. In all cases it is important that the hydrosol droplets not be mechanically disturbed during the gel formation. If considerable water evaporation takes place within the droplets, the structure of the resulting particles will not only be mechanically disrupted during the gel formation, but gas bubbles of considerable sizes, comparable to the size of the particles, will form within them. Accordingly, the medium into which the droplets are introduced should be kept at a temperature that is below the boiling point of the sol.

When gel formation has taken place, a washing operation can take place; in addition, base exchange and finally heat treatment are possible, in order to obtain the desired physical and chemical properties of the gel particles. In these treatments as well, care must be taken that no kind of mechanical damage to the gel particles takes place.

A basic idea of the invention can therefore be seen in the fact that the shape of the particles from the introduction of the droplets into the medium up to the completed drying of the particles is essentially kept constant. The extent of drying is dependent, for example, on how the particles are intended to be used, but in any case the drying is to be carried out to such an extent that shrinkage of the gel particles no longer takes place. The expression "essentially dry" which is intended to characterize this degree of drying, then means more than just dry to the appearance or dry to the touch; it means drying to an extent such that no water will be driven out at a temperature a little above the boiling point of water. At such temperatures the gel particles have

Figure 5 shows fine gel particles.

In Figure 1 a mixing nozzle 10 is put into a water-immiscible liquid in a tank 11 via a column. At the bottom of the tank 11 is a water layer, which forms a separation plane 12 with the upper liquid. Water is continuously supplied through inlet 13 and removed via outlet 14. The separating plane 12 is maintained by the appropriate adjustment of the height of pipe 9 with respect to the density of the liquid and the amount of water supplied at 13. Holes 15 prevent a siphoning effect, and the stream of water carries the gel particles through holes 14 and 9 to suitable washing and treatment devices. The water in which the particles are carried is itself a wash medium and can contain appropriate treatment agents that are intended to have an effect in the further processing.

The colloidal solution from which the particles are to be formed is sent to the liquid column via the mixing nozzle 10. Nozzle 10 is adjusted for complete mixing of two solutions and to feed a continuous stream of the colloidal solution that has been produced under the surface 16 of the water-immiscible liquid, in which the stream of the colloidal solution divides into individual droplets. The colloidal solution can also be fed by drops onto the surface of the liquid, but in this case the droplets can flatten out and control of the droplet size is difficult. With this control, incidentally, care must be taken that significant shrinkage does not occur, not only due to syneresis, but also during the drying and further processing.

The size of the droplets is controlled by the velocity with which the colloidal solution leaves the nozzle opening and through the nozzle size. A simple modification for size control lies in positioning an impact plate at the nozzle outlet. Furthermore, the size is dependent on the specific gravities and viscosities of the colloidal solution and the water-immiscible liquid.

Within mixing nozzle 10 the precisely measured solutions that are to be mixed are passed via tubes 17 and 18 to a chamber, which contains a rotor 19, which is run by shaft 20 at a speed of at least approximately 1700 rpm by means of a power source (not shown). Rotor 19 consists of a four-sided metal rod whose edges are rounded so that the walls of the mixing chamber serve as a guide for it. The rounded edges are provided with grooves, which causes distribution of the two solutions into each other and prevents gel formation in the mixing nozzle. The whole rotor can in general be fluted or the like in any way in order to achieve improved mixing in the mixing zone. Helical grooves for this purpose are shown on rotor 21 in Figure 2. The best action of the mixing nozzle is achieved when the speeds of the reacting solutions are so great that the time within which the solutions are in the mixing chamber is only a very small fraction of the gel formation time.

Another embodiment of a very simple mixer is shown in Figure 3, in which rotor 22 is just a simple shaft, which can be provided with grooves or can be fluted, or the like.

Another embodiment that can be used with the mixing nozzles in Figures 1, 2 and 3 consists of the introduction of air into the solutions that reach the mixing chamber or into the mixing nozzle itself. This produces hydrogel particles that contain many small air bubbles, which serve to make the finished dry gel less dense and more porous.

The plant in Figure 4 is designed for an upwardly directed flow of the colloidal solution during the gel formation. In this case the mixing nozzle 10 is situated at the bottom of the vessel 11, which contains a column of a liquid that is not miscible with water, which is heavier than water and above which is a water layer, so that separation plane 12 results. Water is fed through tube 23 and withdrawn with the gel particles via discharge tube 24. A particular characteristic of the resulting gel particles is their transparency; in many cases they have the appearance of clear glass spheres. This appearance will only be obtained if silica gel is the predominant component; the transparency will be lost when components of other oxides are present in a large measure.

The resulting particles are extraordinarily hard and because of their properties and their smooth surfaces they are resistant to abrasion and shock in use, and thus are more durable than the gel particles known up to now.

#### Example 1

A solution of sodium silicate, which contained 105 g  $\text{SiO}_2$  per liter, was prepared from sodium silicate (28.7%  $\text{SiO}_2$ , 8.9%  $\text{Na}_2\text{O}$ ). This solution was mixed with a second solution, which contained 34.10 g  $\text{Al}_2(\text{SO}_4)_3$  and 26.05 g  $\text{H}_2\text{SO}_4$  per liter, in a ratio of 1 volume of the first solution to 0.780 volumes of the second. The resulting colloidal solution was introduced via a mixing column into the upper part of a column of gas oil about 2.7 m high at room temperature. The droplets of the solution fall through the oil and solidify before they reach the water layer that is under the layer. The gel particles are removed from the bottom of the column in a stream of water and after separation from the water are washed with petroleum in order to remove all of the oil from their surface. They were then washed with water and  $\text{NH}_4\text{Cl}$  solution in order to replace zeolitically bonded sodium ions by ammonium ions, which are capable of being driven out as  $\text{NH}_3$  gas by heat. The gel particles were slowly and evenly dried at  $82^\circ$  until shrinkage was essentially completed, and then the drying was continued at a gradually rising temperature to  $565^\circ$ , which was maintained for 2 h. The silicic acid-alumina gel retained its spherical shape during the washing and drying. On the other hand, the hydrogel particles can be dried without shrinking by replacing the original liquid fraction (water) by a liquid with relatively low critical temperature such as, for example, alcohol, heating it to the critical temperature, while maintaining pressure sufficiently high to keep the alcohol liquid, and letting the evaporation of the alcohol take place at a temperature above the critical temperature.

For the above concentrations and reactant ratios the gel formation time was about 10 sec, while the pH was 6.9. The gas oil that was used was a fraction of Oklahoma City gas oil with a boiling range from 244-375° and a specific weight of 0.846.

### Example 2

Chlorobenzene was used as the liquid medium in this case and the mixture of the reactants was adjusted in its concentrations and proportions so that the gel formation time was roughly 20 sec, while the pH amounted to 6.9. Since chlorobenzene has a density of 1.101, the colloidal solution was introduced from below into a 3.3-m-high liquid column of chlorobenzene at room temperature (see Figure 4), and the droplets rose through the liquid upward and solidified before they reached the water layer over the chlorobenzene. The gel was washed and dried as given in Example 1 (the washing with petroleum was not necessary in this case).

The sodium silicate solution contained 105 g  $\text{SiO}_2$  per liter (prepared as sodium silicate as in Example 1), while the second solution contained 27.10 g  $\text{Al}_2(\text{SO}_4)_3$  and 19.95 g  $\text{H}_2\text{SO}_4$  per liter. This solution was mixed in a ratio of 1 volume of the first solution to 0.980 of the second.

### Example 3

This Example 1s concerned with the preparation of spherically shaped silica gel particles and their conversion to a cracking catalyst. The gel formation time for the concentrations and proportions of the reactants given below was roughly 30 sec, while the pH was 5.7.

A plant as in Figure 1 was used in the preparation of this gel. A solution of sodium silicate that contained 106.3 g  $\text{SiO}_2$  and 33.0 g  $\text{Na}_2\text{O}$  per liter and that was prepared by diluting sodium silicate as before was precisely measured and continuously fed via inlet 18 of the mixing chamber, while a measured solution of 3.90 normal hydrochloric acid was continuously introduced via inlet 17. The reacting solution was mixed in a ratio of 3.34 volumes sodium silicate solution to 1 volume acid solution. The resulting colloidal solution went from above into a 3-m-high liquid column of petroleum oil that was at room temperature and had a viscosity of about 66 cSt and a specific weight of 0.891. The droplets of the solution fall through the oil and solidify before they reach the water layer that is under the oil. The spherically shaped hydrogel was withdrawn from the bottom of layer 11 via a water stream with the aid of pipes 14 and 9. The hydrogel was washed with benzene in order to remove the oil film and then with water until it was free of sodium chloride. The washed hydrogel was put overnight in a 25% solution of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and then the excess of the solution was poured off. The spherically shaped silicic acid hydrogel, which was impregnated with aluminum nitrate, was slowly dried at 82° until shrinkage was essentially complete, and the drying was continued with gradually increasing temperature up to 565°, which was maintained for 2 h. The aluminum nitrate was converted to

the oxide during the heating and thus a silicic acid-alumina gel catalyst was obtained in the form of spherical particles with good activity.

The hydrogel particles that were obtained in accordance with Examples 1, 2 and 3 had diameters of approximately 5 mm, and there were no problems in the drying and shrinkage to their end form. Nevertheless, it was found that in the case of the hydrogel particles of the order of 8 or 10 mm in diameter considerable breakage and cracking of the particles takes place if they are rapidly dried. This can be prevented if the particles are treated with boiling water or steam for 15-30 min before drying.

The spherical particles in accordance with Example 1 were compared with particles produced in the usual way by means of hardness tests. Comparison of the cracking effect shows that the prepared particles essentially have the same effect as molded particles and pieces produced by breaking. A silicic acid-alumina hydrogel was prepared by mixing the reactants in the same concentrations and proportions as in Example 1. This mixture was allowed to solidify as an integral mass in the usual way.

The hydrogel was divided into two parts after washing, drying one part and then size reducing it to obtain broken pieces of the desired size; the other part of the hydrogel was poured into molds and dried in order to produce small cylindrical particles. These two forms were subjected to hardness tests, as have been developed for cracking catalysts, where a certain amount of particles is stirred or shaken for one hour in a can and then screened to determine the size reduction factor. The particles produced by breaking the gel showed a size reduction of 12% in one test, while the cylindrical particles were broken in an extent of 6%. The greater value of the particles produced by breaking probably comes from their irregular shape and is a consequence of impact and fracturing during the size reduction.

The particles in accordance with Example 1 did not show any pulverization or size reduction in the test. An extension of the test to 15 h showed only scratching of the surface of the particles, which resulted in only a small amount of abrasion. An 80 h test produced only 0.3% material that was smaller than the original material. The particles in accordance with the invention in general showed losses of less than 1% per hour in these tests; the best particles showed losses of less than 0.25% per hour.

The particles in accordance with the invention can also be used as carriers for other substances, in a substantially known way.

The size of the gel particles in accordance with the invention is dependent on how the colloidal solution divides into individual droplets. This is again a function of a number of variables. The most important is how the colloidal solution is introduced and what the surface tension is between the colloidal solution or the droplet and the immiscible fluid through which the droplets pass. The size of the particles can also be influenced through the type of drying,



since specifically the shrinkage during the drying derives from the capillary action at the meniscus of the liquid phase when this phase retreats through the porous gel structure. The particles can be obtained as large as one desires, but for most purposes, especially for catalytic hydrocarbon conversion, the maximum sizes are about 10 mm in diameter. Advantageously, the particles are from 3-7 mm, where it turns out that 5-mm particles are generally useable.

Much smaller particles can be formed for particular requirements. If, for example, a catalyst is to be suspended in reaction gases, particles with an average diameter of less than 0.1 mm can be produced. Nozzles with small orifices are advantageously used when the gel formation takes place in a liquid medium. For example, any of the nozzles that are shown can be made smaller at the outlet or can be provided with a plate at the outlet that has a number of small poles. Small orifices of this kind can, however, frequently produce deposits of gel in the nozzle and give rise to the need for frequent cleaning. This is advantageously avoided essentially by making a colloidal solution that takes several minutes to solidify at room temperature and then feeding this sol from the mixing nozzle into an oil mass at elevated temperature. The heating of the sol droplets accelerates the gel formation in order to obtain practical gel formation time, while gel formation in the nozzle is prevented. A method of this kind is described in the following example.

#### Example 4

A water glass solution was prepared by diluting 12.4 kg sodium silicate with 7.9 L water. The solution contained 212 g  $\text{SiO}_2$  and 66 g  $\text{Na}_2\text{O}$  per liter. A second solution was prepared by dissolving 387 g sodium aluminate in water to form 10 L of solution. These two solutions were mixed in a ratio of 100 volumes of the first solution to 67.8 volumes of the second. The sodium aluminate-sodium silicate solution was mixed with 1.224 normal hydrochloric acid in equal volumes in the nozzle mixer immediately after preparation in order to form a colloidal solution with a pH of 5.7 and a gel formation time of 3 min at room temperature. The colloidal solution was fed from the nozzle mixer into the upper part of a gas oil layer that was 4 m deep and that was kept at a temperature of  $98^\circ$ . The sol droplets fall through the oil and solidify before they reach the water layer, which is situated under the oil. Washing and drying of the hydrogel were carried out as in Example 1.

This is the preferred preparation of particles with a diameter smaller than 0.1 mm. Meanwhile, particles of any desired size can be prepared by this embodiment. Colloidal solutions that are prepared in accordance with the invention and whose gel formation times at room temperature amount to more than a few minutes and up to a few hours can be converted to spherical particles by heating the sol for a predetermined period of time and then introducing it in

the form of droplets into a body of oil at elevated temperature, in which the sol droplets solidify. This method is described in the following example.

#### Example 5

A sodium aluminate-sodium silicate solution prepared as in Example 4 was mixed in a nozzle mixer with 3.780 normal hydrochloric acid solution in an amount of 100 parts by volume of the first solution and 32.6 parts by volume of the acid solution in order to prepare a sol with a pH value of 3.4 and a gel formation time of 2 h at room temperature. The colloidal solution leaving the mixing chamber was pumped through a tubular coil in a 70° bath for heating. The sol remained in the coil for 120 sec before it was introduced in the form of droplets into the upper part of a gas oil layer that was 4 m deep and was maintained at 95°. The droplets of the colloidal solution fall through the oil and solidify before they reach the water layer under the oil. The hydrogel particles were washed and then dried as in Example 1.

Small particles are also obtained by size-reducing the particles to any desired size. It was found that the gels maintain their hardness and likewise their high density after such size reduction. It was further found that a certain change in the apparent density derives from the denser layering of the particles. In practical production a considerable part of the product will be seen as waste, either because the particles do not have the desired size or are broken. This waste is well suited for the production of a hard gel by grinding, etc.

The formation of particles in accordance with the invention in a gaseous medium is illustrated by the following example.

#### Example 6

An acid solution was prepared by mixing 3.5 parts by weight 100% sulfuric acid, 7.9 parts by weight commercial iron-free aluminum sulfate with 15 molecules of water per molecule of salt and 88.6 parts by weight distilled water. A dilute water glass solution was prepared by mixing 44.7 parts by weight distilled water and 55.3 parts by weight sodium silicate (28.7% SiO<sub>2</sub>, 8.9% Na<sub>2</sub>O). These solutions were mixed in a nozzle mixer of the type shown in the drawing, in an amount of 137 parts by volume acid and 150 volumes of water glass, with the formation of a sol, which in less than 1 sec converted to a solid hydrogel with 10 g silicic acid and alumina to 100 g of gel. Immediately after mixing, the gel was injected at room temperature through an orifice into a larger vessel that contained air at room temperature. The resulting injection stream converted to small droplets of hydrogel, which were collected in a water layer at the bottom and after being removed were washed. Base exchange with 3% aluminum sulfate solution was then carried out; then washing and drying were again carried out as in the previous examples. The product consisted of small hydrogel particles with a cracking activity of 52.7%, as

shown later, and with physical properties that, apart from size, are essentially the same as those of the larger particles that were formed in a liquid according to the preceding examples.

The particles in general have spherical form. Usually they are somewhat flattened and approach an ellipsoidal form. The irregularities in shape and size in practical production greatly resemble rounded pebbles in a streambed, only the particles are naturally much smaller. For this reason the best definition of the shape appears to be given by the term "rounded particles," which characterizes solid particles that have only smooth curved outer surfaces and that essentially do not have any flats or edges. In addition, the surfaces of the spherical particles usually also are very smooth, and resemble glass with regard to smoothness and luster, which is due to the method of their manufacture, in contrast to broken surfaces. The similarity to glass is further increased through the way these particles fracture and their transparency. The fracture is characteristically shell-shaped and the particles are translucent to transparent, which is dependent on the type of formation, for example on the concentration and pH of the colloidal solution, on the type of treatment, etc. This is a notable contrast to the synthetic gel particles obtained by molds, which essentially have the appearance and physical properties of chalk, although they are somewhat harder than chalk.

The surfaces (both the original surface and fracture surfaces) of these particles are extraordinarily hard because of their chemical and physical nature. Precipitated silica gel is normally soft and the highly porous nature of the particles would leave one to expect that the particles have surfaces that are easily scratched. Surprisingly, the surfaces have a hardness in the same range as glass. The preferred types vary in hardness from about less than 4 on the Mohs scale up to 6 and harder. In practical production it is easy to produce particles that scratch hardened glass. The advantages of such hardness are clear, especially when, as in this case, they are linked with a smooth surface. When used for catalytic conversion of hydrocarbon, the particles of the catalytic substance are, for example, either packed in a fixed bed or continuously moved through a treatment chamber or suspended in the gas that is to be treated. In a continuous process the particles are in constant motion and subject to continuous abrasion. Smooth hard surfaces like those of these particles resist abrasion, while the soft rough surfaces of the particles that were used earlier rapidly crumble and produce an undesired fine abrasion, through which the catalyst is consumed. Even in the case of fixed beds the particles are subject to destructive forces. The particles have to be loaded into the container and blowing gases and changing pressures during operation produce movement of the particles in the catalyst bed and this produces undesired abrasion.

The strength of the particles is extraordinarily high. Individual particles produced by the described method easily withstand over 22.5 kg. They are tested by placing an individual particle on a base and applying a pressure directly to the upper surface of the particle until it breaks. A

particle strength measured in this way of over 45 kg is preferred and strengths of 135 kg are not unusual for normally prepared particles. A comparison with particles of the same chemical composition obtained by using molds is of interest. These molded particles break at a weight of about 2.25 kg. It is possible with molding at high pressure to achieve a strength of about 9 kg as a maximum, but molding under pressure is not feasible in practical terms. The disintegration strength of particles in a mass is likewise extraordinarily high. Normal particles in accordance with the invention in mass resist pressures of over  $70 \text{ kg/cm}^2$ , and it is preferred that the mass of particles should resist at least  $140 \text{ kg/cm}^2$ . Batches of particles have been prepared that in mass resist a pressure of  $210 \text{ kg/cm}^2$  and higher. For comparison one should note that industrially molded silica gel catalyst in mass breaks apart at pressures of  $35 \text{ kg/cm}^2$ , while the fracture of particles of silica gel catalyst in mass break apart under pressures of  $7 \text{ kg/cm}^2$ .

The hardness and strength of this catalyst also follows from a test in which the catalyst is forced through a tube in an air stream and then ejected against a vertical steel plate. Fine particles are withdrawn from above, while larger parts of the catalyst fall into a collection vessel and return to the air stream. Circulating a catalyst made of molded particles for a period of 15 h produced 46% fine particles, while none of the catalysts in accordance with this invention produced more than 5% fine particles. The preferred catalysts show extraordinarily low losses, for example 0.1% in the case of the catalyst in accordance with Example 1.

On the interior these gel particles essentially have the structure of the original hydrogel after removal of the liquid fraction. The size of the particles is naturally reduced during normal drying and the structure is probably somewhat deformed to a degree that corresponds to the deformation of the particle as a whole. Meanwhile, for all practical purposes the original gel structure is completely retained with the dried gel particles. Additionally, it is important that the prepared gel particles are uniformly porous, in contrast to the molded particles, in which a part becomes poorly molded during molding, so that the porous structure is partially lost.

The apparent density of the product varies in the same direction as the resistance to size reduction, but it is not simply a function of the apparent density. The term "apparent density" is intended to indicate the weight with respect to the volume that is taken up by the mass of the particles. It is determined by weighing a measured large volume of particles. For example, a large diameter cylinder provided with a measurement scale is filled with particles up to a specific measurement mark, and the weight of the particles is determined from the difference of the weight of the measurement cylinder before and after filling it. In general, the apparent density of these particles varies between  $0.5$  and  $1.1 \text{ g/cm}^3$ . Lighter particles with apparent densities as low as  $0.3 \text{ g/cm}^3$  can indeed be made, but their hardness and resistance to breakage are low. Apparent densities over  $0.7 \text{ g/cm}^3$  are preferred. For comparison, molded gel particles usually have an apparent density of about  $0.55 \text{ g/cm}^3$ . Higher densities up to about  $0.75 \text{ g/cm}^3$  are possible only

with molding at high pressure. An interesting inverse relationship between the apparent density and composition of the gel particles was established. When silicic acid-alumina gels were produced by mixing sodium aluminate, water glass and a mineral acid, increasing apparent densities allowed a reduction of the alumina content for the same activity. Oddly enough, this rule does not apply when the colloidal solution that is supposed to solidify is obtained by mixing aluminum sulfate and water glass to obtain a colloidal solution with the same pH, silicic acid content and alumina content. The following table shows this peculiar relationship. The table shows activities and compositions in % by weight with respect to dry substance of a batch of  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  gel catalyst particles that were prepared by mixing sodium aluminate, water glass and sulfuric acid.

//insert table//

Key: 1 Catalyst composition  
 2 Apparent density  
 3 Activity  
 4 of catalyst

The activity of the catalyst is the measure of its effectiveness in the catalytic conversion of hydrocarbons and here is expressed as the percent conversion of Oklahoma City gas oil with a specific weight of 0.845 and a boiling range of 243.5-375.5° to gasoline with an end boiling point of 210°, by passing gases of this gas oil through the catalyst at 426.5° at approximately atmospheric pressure and in an amount of 1.5 volumes of liquid oil per volume of catalyst per hour with 10 min of operation between regenerations.

The activity is a relative property that can be precisely applied only in reference to a particular conversion under particular conditions. Thus, catalysts suitable on the basis of this test do not in general have lower activities than about 5.0%. It is clear that a 5% conversion to gasoline is not a good economic process, but this test is not intended to report a maximum or minimum of activity, but rather only to be a basis for comparison for evaluation of catalysts. It

would be extraordinarily difficult to report an activity on another basis as a standard, since the conversion varies with the nature of the starting material and the conditions during processing. In general, the conversion of the gas oil to gasoline increases with elevated temperature or pressure. A less active catalyst in general gives quite good yields under more severe conditions. A typical low-activity catalyst, on the basis of this test, is a silicic acid-alumina catalyst with an activity of 5% in the above test; however, a conversion in the order of 30% can be achieved with the same starting material, the same pressure and the same quantity if the temperature is 482-510°.

Catalysts for the conversion of hydrocarbon should have activities of about 5% or more according to the above test, while for general purposes (i.e., use in a wide range of conversion conditions) catalysts with activities of at least 20% are desired. Preferably, the catalyst should have an activity of not less than 40%.

The density of the catalyst per se is an important property for these purposes. With any kind of catalytic conversion of hydrocarbons some of the solid catalyst is carried out by the converted vapor. When the preferred spherical catalyst in accordance with the invention is used as a fixed or moving bed, the amount of this entrained fine particles is extraordinarily small, and it can even be permissible that they depart with these vapors to be collected with the tarry residues after separation of the lighter more valuable hydrocarbons. When in the meanwhile it is desirable to separate the entrained fine catalyst particles or in the case of processes in which the catalyst is suspended in the vapors, separation is a considerable problem. The higher densities of the preferred catalysts in accordance with the invention enable rapid separation of the finely divided material. These preferred catalysts have apparent densities of somewhat over 0.7 g/cm<sup>3</sup>.

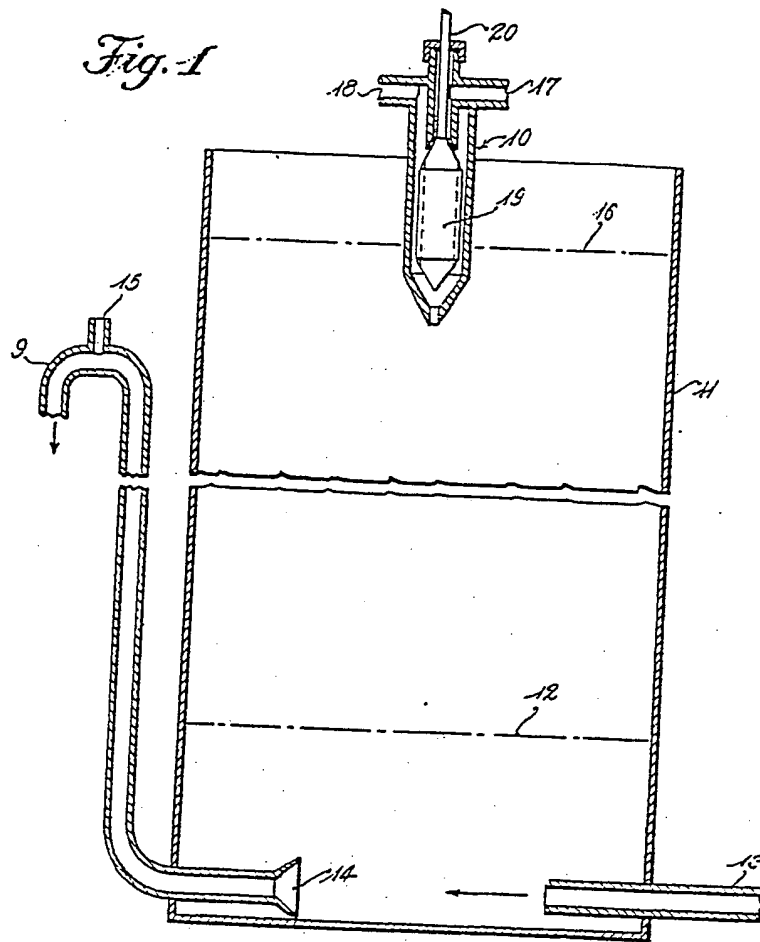
The density also affects temperature control when using the catalyst masses. For regeneration of the spent catalyst in the case of hydrocarbon conversions the carbon-containing deposits are burnt out with preheated air. In some cases provisions must be made that the heat that arises in this highly exothermic reaction is removed in order to avoid adverse effect on the catalyst. The denser catalyst now has a higher heat capacity per unit volume and can itself for this reason accommodate more heat without suffering damage due to heat, so that the strain on other heat-regulating parts in the plant is reduced.

### Claims

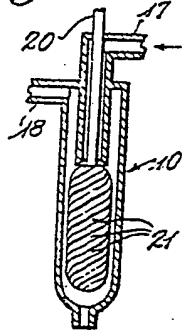
1. A method for producing silicic acid-containing gel particles with adsorbent and catalytic properties from a gel-forming hydrosol of an inorganic oxide, which is characterized by the fact that the sol, while being divided into individual droplets and taking on a more or less spherical shape, is introduced into a medium that is not miscible with water or the hydrosol, that is kept at a temperature under the boiling point of the sol, and in which the droplets remain until gel formation is complete.

2. A method as in Claim 1, which is characterized by the fact that the sol is introduced from above into a mineral oil layer, which is on top of a water layer, so that the droplets pass through the oil layer by gravitational force and in doing so gel formation takes place, while the formed gel particles after they enter the water layer are removed by a flow of water within this layer.
3. A method as in Claim 1, which is characterized by the fact that the sol is introduced from below into a liquid layer, which is heavier than water and which is under a water layer, so that the droplets rise upward through the lower layer and in doing so gel formation takes place, while the formed gel particles, after reaching the water layer, are removed by a flow of water within this layer.
4. A method as in Claims 1-3, which is characterized by the fact that the gel particles are washed and/or dried after being removed from the liquid or gaseous medium.
5. A method as in Claims 1-4, which is characterized by the fact that sodium silicate in a mixture with an acid solution is used as the gel-forming hydrosol.
6. A method as in Claims 1-5, which is characterized by the fact that the mixing of, for example, sodium silicate and the acid solution takes place in a mixing nozzle, from which the sol droplets go directly into the water-immiscible medium, by inserting the mixing nozzle into the medium.

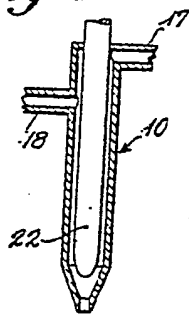
*Fig. 1*



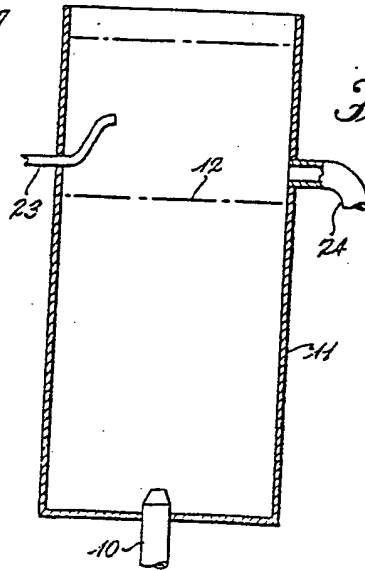
*Fig. 2*



*Fig. 3*



*Fig. 4*



*Fig. 5*

